Global change effects on the long-term feeding ecology and contaminant exposures of East Greenland polar bears

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Abstract

Rapid climate changes are occurring in the Arctic, with substantial repercussions for arctic ecosystems. It is challenging to assess ecosystem changes in remote polar environments, but one successful approach has entailed monitoring the diets of upper trophic level consumers. Quantitative fatty acid signature analysis (QFASA) and fatty acid carbon isotope (δ^{13}C-FA) patterns were used to assess diets of East Greenland (EG) polar bears (*Ursus maritimus*) (n = 310) over the past three decades. QFASA-generated diet estimates indicated that, on average, EG bears mainly consumed arctic ringed seals (47.5 ± 2.1%), migratory subarctic harp (30.6 ± 1.5%) and hooded (16.7 ± 1.3%) seals and rarely, if ever, consumed bearded seals, narwhals or walruses. Ringed seal consumption declined by 14%/decade over 28 years (90.1 ± 2.5% in 1984 to 33.9 ± 11.1% in 2011). Hooded seal consumption increased by 9.5%/decade (0.0 ± 0.0% in 1984 to 25.9 ± 9.1% in 2011). This increase may include harp seal, since hooded and harp seal FA signatures were not as well differentiated relative to other prey species. Declining δ^{13}C-FA ratios supported shifts from more nearshore/benthic/ice-associated prey to more offshore/pelagic/open-water-associated prey, consistent with diet estimates. Increased hooded seal and decreased ringed seal consumption occurred during years when the North Atlantic Oscillation (NAO) was lower. Thus, periods with warmer temperatures and less sea ice were associated with more subarctic and less arctic seal species consumption. These changes in the relative abundance, accessibility, or distribution of arctic and subarctic marine mammals may have health consequences for EG polar bears. For example, the diet change resulted in consistently slower temporal declines in adipose levels of legacy persistent organic pollutants, as the subarctic seals have higher contaminant burdens than arctic seals. Overall, considerable changes are occurring in the EG marine ecosystem, with consequences for contaminant dynamics.

Keywords: contaminants, diet, fatty acid carbon isotopes, fatty acids, polar bear, sea ice, temporal trends

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Introduction

Although the magnitude of arctic warming is two to three times the global rate of change and has resulted in staggering sea ice loss (Perovich & Richter-Menge, 2009), it is challenging to assess the repercussions of these changes on remote polar marine ecosystems (Wassmann *et al.*, 2011). One successful approach has been to monitor the diets of upper trophic level consumers. For example, thick-billed murre (*Uria lomvia*) diet changes from mostly arctic cod (*Boreogadus saida*) to mostly capelin (*Mallotus villosus*) are thought to

represent a major ecosystem shift from arctic to subarctic marine forage fish within the eastern Canadian Arctic from the 1970s–1980s to the 2000s (Provencher *et al.*, 2012). Similarly, polar bear (*Ursus maritimus*) diets are expected to change in response to climate-induced shifts in the abundance or distribution patterns of arctic and subarctic marine mammals (Stirling & Parkinson, 2006).

Biochemical tracer techniques have recently provided time-integrated assessments of polar bear diets. One technique, fatty acid (FA) analysis is based on the knowledge that many FAs consumed by monogastric species are deposited in storage tissues in similar proportions to their diet (Budge *et al.*, 2006). Polar bear FA signatures have been compared among circumpolar

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subpopulations and over time to suggest spatial and temporal dietary trends, respectively (McKinney *et al.*, 2009, 2011). An extension of this approach, called quantitative FA signature analysis (QFASA), statistically compares predator FA signatures to those of potential prey to generate diet estimates (Iverson *et al.*, 2004), and has been used to quantify subpopulation differences and limited temporal variation in diets of Canadian arctic and subarctic polar bears (Iverson *et al.*, 2006; Thiemann *et al.*, 2008a).

Analogous to FA signatures, stable isotopes of certain elements (e.g., commonly used nitrogen and carbon isotopes) occur at similar ratios in predators and prey, or at least at predictably different ratios (Post, 2002). Whole tissue bulk nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) stable isotope ratios have been used to infer trophic level and carbon sources, respectively, of individual polar bears and subpopulations, as well as temporal changes (McKinney *et al.*, 2009, 2011; Knott *et al.*, 2011; Dietz *et al.*, 2013a). This bulk method represents the average isotope ratio for all individual biomolecules in a sample. Another promising diet analysis approach, compound-specific isotope analysis (CSIA), is potentially more sensitive than bulk isotopes or FA analysis alone (Hayes *et al.*, 1990; Evershed *et al.*, 2007). The most common CSIA method, although still rarely employed and not as yet for polar bears, involves measuring $\delta^{13}C$ values of individual FAs. An individual FA may be at similar proportions in different food sources, but have distinct $\delta^{13}C$ values, so including this approach in food web studies may reduce ambiguity that can occur based on overlapping FA signatures or bulk isotope ratios. However, $\delta^{13}C$-FA ratios may also be influenced by isotope fractionation during metabolism and biosynthesis (Budge *et al.*, 2011).

The East Greenland (EG) polar bear subpopulation is within the convergent ice ecoregion (Amstrup *et al.*, 2008). Ice formed in other regions tends to converge in this region, generally providing the EG subpopulation with year-round access to sea ice and thus to marine mammal prey. Convergent ice polar bear subpopulations may initially be less affected by ice loss than those in seasonal and divergent ice ecoregions, but are nonetheless predicted to be extirpated within 75 years (Amstrup *et al.*, 2008; Stirling & Derocher, 2012). In fact, the ice loss rate of 9.8%/decade for the Greenland Sea is one of the most rapid in the Arctic (Perovich & Richter-Menge, 2009). The EG polar bear subpopulation, based on marine mammal polar distributions (reviewed in Laidre *et al.*, 2008), has year-round access to arctic ringed seals (*Pusa hispida*), bearded seals (*Erignathus barbatus*), walruses (*Odobenus rosmarus*) and narwhals (*Monodon monoceros*), and seasonal access to migratory, subarctic harp seals (*Phoca groenlandica*) and

hooded seals (*Crystophora cristata*). Tracking data from central EG polar bears indicated that they were "off-shore" bears inhabiting the pack ice within harp and hooded seal whelping/molting areas from spring until mid-late summer (Wiig *et al.*, 2003; Laidre *et al.*, 2013). An influx of harp and hooded seals may occur in a warming arctic, coinciding with northward retractions of arctic seals and their prey (Laidre *et al.*, 2008). The diets of EG polar bears thus provide an opportunity to examine whether such ecosystem changes have occurred in this region as the climate has warmed and the sea ice has declined over the past three decades (Perovich & Richter-Menge, 2009).

A shifting diet may have health consequences for EG polar bears. For example, subarctic seals may be vectors for transporting contaminants from temperate/subarctic regions to the Arctic (Kleivane *et al.*, 2000; McKinney *et al.*, 2012). The EG polar bear subpopulation has shown overall declining legacy persistent organic pollutant (POP) levels (average 4.4% yr^{-1}) between 1983 and 2010 as a result of international regulations, but this decline stopped around 2000 and relatively high legacy POP levels still occur (e.g., PCBs, chlordanes) (Dietz *et al.*, 2013b). Other contaminants including brominated flame retardants have increased (5% yr^{-1}) in EG polar bears, as well as perfluorinated compounds, over the same three decades (Dietz *et al.*, 2008, 2013a). Finally, a growing body of evidence from correlative studies in polar bears and controlled studies in model arctic carnivore species suggests that current POP and mercury levels in these highly exposed EG polar bears are contributing to subclinical reproductive and immune-related health effects (Letcher *et al.*, 2010; Sonne, 2010).

Here, we use QFASA and $\delta^{13}C$-FA patterns to provide the first evidence of long-term (1984–2011) changes in EG polar bear diets, which reflect broad scale changes in the EG ecosystem. We relate diet changes to regional (Greenland Sea ice area) and large-scale climate indexes (North Atlantic Oscillation; NAO). We also determine potential consequences of EG diet changes on POP temporal trends.

Materials and methods

Sample collection

Adipose tissue samples were collected from 310 EG polar bears harvested between 1984 and 2011. Samples were collected by Aarhus University researchers and subsistence hunters near Ittoqqortoormiit (Scoresby Sound) at ca. 69–74°N off the central east coast of Greenland. Additional collections from the same area included blubber samples of 15, 5, and 30 ringed seals (2002, 2004 and 2006, respectively), and 2 narwhals and 2 walruses (2010 and 2011, respectively), while

8 bearded seals samples were taken from south Greenland (Cape Farewell area) in 2011. Samples were kept frozen after collection and during transport, and at ≤−20 °C for long-term storage. To improve sample sizes and include all potential prey species, additional prey data from within a neighboring subpopulation region (see Diet estimation by QFASA) were included in the prey fatty acid database.

Polar bears were aged by counting annual growth layer groups from the cementum of a lower right I3 tooth (Dietz *et al.*, 2004) and classified by sex/age as adult males (≥6 years), adult females (≥5 years) and subadults (all other bears) (Rosing-Asvid *et al.*, 2002). Bears were also classified by season of collection, i.e., spring-summer (February–July) and fall-winter (August–January of the following year).

Fatty acid analysis

Polar bear and prey adipose/blubber FA analysis proceeded as detailed elsewhere (Thiemann *et al.*, 2008a). Although the dataset included samples archived for three decades, long-term archiving (−20 °C, 6 year) of even small biopsy samples appears to have no major effect on FA signatures (Lind *et al.*, 2012). Nonetheless, to avoid potentially oxidized outer tissues, we subsampled the innermost tissue of the available samples. To investigate the potential influence of oxidation on the diet estimates, we classified each subsample according to visual extent of oxidation ("subjective oxidation class") on a 1–5 scale: 1 = white/fresh; 2 = mainly white/slight yellow tinge; 3 = white-yellow; 4 = mainly yellow/slight white tinge; 5 = yellow/sometimes a bit dry. Lipid was then extracted twice using 8:4:3 chloroform:methanol:water, containing BHT as antioxidant, at a volume:weight ratio of 20:1 solvent:sample. FAs were derivatized to FA methyl esters (FAMEs) using methanol containing 0.5 N H_2SO_4. FAME extracts (50 mg/ml total FAME) were analyzed in duplicate on a Varian CP-3800 gas chromatograph with flame ionization detection (GC-FID) using a DB-23 column (Agilent Technologies, Palo Alto, CA, USA). FAs were quantified as mass percent of total FAME. The FA nomenclature, x:yn-z, indicates carbon chain length x, number of double bonds y, and position of the first double bond counting from the methyl end of the chain z.

Fatty acid carbon isotope analysis

We performed δ^{13}C-FA analysis on 111 polar bear FAME extracts (from the *FA analysis* above) from samples of subjective oxidation class 1 (all from 1986 to 2010) to minimize potential δ^{13}C-fractionation that could occur during FA oxidation/degradation reactions. We also performed δ^{13}C-FA analysis on 5 randomly selected ringed seal extracts from each of 2002, 2004, and 2006. Extracts were analyzed on a Trace GC Ultra coupled via a GC Combustion II/III Interface to a Delta V Advantage isotope ratio mass spectrometer (GC-C-IRMS) (Thermo Scientific, Waltham, MA, USA). The GC column and temperature program were the same as for FA analysis. However, samples were injected in splitless mode to prevent fractionation in the inlet, and thus run at lower concentrations of 0.5 and 2.0 mg/

ml total FAME. Running at two concentrations allowed us to check reproducibility, obtain more analyte peaks within the IRMS linear range (ca. 600–6000 mV for m/z 44 amplitude), and avoid excessive co-elution that occurs at higher concentrations. Five saturated FAME standards of known δ^{13}C [16:0 (#n16M), 20:0 (#x), 18:0 (#n18M), 20:0 (#2) and 24:0, ranging from −30.68‰ to −6.91‰; Biogeochemical Laboratories, Indiana University, Bloomington, IN, USA] were run weekly at serial dilutions of ca. 125, 62.5, 31.25, 7.81 μg/ml. The 31.25 μg/ml standards were run daily to generate a calibration curve ($r^2 \geq 0.993$) for calculating δ^{13}C-FAME of samples. To avoid bias from co-elution occurring for certain peaks run by GC-C-IRMS, the 18:1, 20:1 and 22:1 isomers were each integrated as single peaks representing the sum of each isomer group. Only well-separated FAs within the linear range for ≥70% of samples at one or both concentrations were reported: 14:0, 16:0, 16:1n-7, 18:1, 20:1, 22:1, 20:5n-3, and 22:6n-3.

Values of δ^{13}C for the methanol (Fisher Scientific, Optima Grade, Lot #100360) used to derivatize FAs to FAMEs were determined by EA-IRMS using manual liquid injection (Environmental Isotopes Lab, University of Waterloo, Waterloo, ON, Canada). Values of $\delta^{13}C_{FAME}$ and average $\delta^{13}C_{methanol}$ (−51.01‰) were used to calculate by mass balance the individual $\delta^{13}C_{FA}$:

$$(n + 1)\delta^{13}C_{FAME} = n(\delta^{13}C_{FA}) + \delta^{13}C_{methanol}$$

where methanol adds one carbon atom to the FA of carbon chain length n to create the FAME of carbon chain length $n + 1$.

Climate indexes

We used Greenland Sea ice area as a regional climate index. Data were obtained from 1984 to 2010 from the National Snow and Ice Data Center using the NASA Team Algorithm (Cavalieri *et al.*, 1996). Ice area is calculated as the area of each pixel >15% ice concentration multiplied by the fractional ice concentration in the pixel (0.15–1.00), and so accounts for both ice extent and concentration. Monthly values from each year were averaged to obtain an annual ice area index.

The NAO is a large-scale climate index defined as the normalized air pressure gradient at sea level between Iceland and the Azores (Hurrell, 1995). A positive NAO is characterized by a strong cyclonic wind field over the Arctic, which transports more ice through Fram Strait and into the EG Current. This results in below average temperatures and more arctic ice in EG. Opposite patterns are seen during negative NAO periods. Monthly mean 1984–2011 NAO data obtained from the National Oceanographic and Atmospheric Administration's Weather Service, Climate Prediction Centre (http://www.cpc.ncep.noaa.gov/products/precip/CWlink/pna/nao.shtml) were used to calculate an annual NAO index.

Contaminant analysis

POP analysis in these EG polar bear adipose samples is described elsewhere (Appendix S1: Dietz *et al.*, 2013a,b). Here, we focused on the 15 highest concentration individual and sum (∑) POPs previously reported (Dietz *et al.*, 2013a,b) and that had no nondetect values: ∑PCB; PCB congeners CB153,

CB180, CB170/190; hexachlorobenzene (HCB); octachlorostyrene (OCS); α-hexachlorocyclohexane (α-HCH); ∑dichlorodiphenyltrichloroethane (∑DDT); DDT metabolite p,p'-DDE; dieldrin; chlordanes (CHLs) oxychlordane, t-nonachlor, heptachlor epoxide; ∑polybrominated diphenyl ether (∑PBDE); and PBDE congener BDE153.

Quality control

Quality control for all analyses was assessed by analysis of appropriate blanks, duplicates, and standard reference materials (Appendix S1).

Diet estimation by QFASA

The QFASA approach assumes that the predator FA signature, after correcting for differential metabolism and deposition, represents the weighted combination of the FA profiles of its various prey. This technique has been described previously (Iverson *et al.*, 2004), and in detail for polar bears (Iverson *et al.*, 2006; Thiemann *et al.*, 2008a). Briefly, here the predator FA dataset initially consisted of all 310 EG polar bears from 1984 to 2011. For modeling, we used 31 'dietary' FAs present entirely or primarily from direct dietary uptake (Iverson *et al.*, 2004). Polar bear 'dietary' FAs were corrected using predator-specific calibration coefficients (CCs) generated from mink (*Mustela vison*) fed controlled marine diets (Iverson *et al.*, 2006; Thiemann *et al.*, 2008a). The prey FA library was generated from the Greenland prey, augmented with a prey library from within Davis Strait, an adjacent polar bear subpopulation range (date from Thiemann *et al.*, 2008a,b). The combined library ($n = 509$) comprised the average FA signature of each prey species based on 55 bearded seals, 239 harp seals, 32 hooded seals, 22 narwhals, 106 ringed seals, and 55 walruses. QFASA was used to determine the proportion of prey species signatures that best matched each individual polar bear signature by minimizing the statistical distance over all 'dietary' FAs between the prey signatures and the CC-corrected polar bear signatures (Iverson *et al.*, 2004). The model was run in R (R Development Core Team, 2011). The standard error of the diet estimates was calculated from the between-bear standard error, i.e., variation in diet estimates among bears. Within-bear standard error, i.e., variation resulting from FA signature variability among individuals of a particular prey species, was not considered as it is small relative to between-bear standard error and does not substantially influence diet estimates (Thiemann *et al.*, 2011).

Simulation studies were run to determine the robustness of the model (Iverson *et al.*, 2004). First, prey-on-prey modeling assessed how distinct the individual prey species FA signatures were from one another (Appendix S1). A second simulation assessed how well QFASA modeling estimated diets relative to a simulated diet (Appendix S1). To investigate the robustness of diet estimates to spatial and temporal variation in the prey library, we compared prey FA profiles from this and other published studies consisting of marine mammals collected at different locations and times. We also performed a hierarchical cluster analysis (using squared Euclidean dis-

tances and the unweighted pair-group average linkage method) using the average of each dietary FA from the entire prey library used to estimate EG polar bear diets. Finally, we compared EG polar bear diets estimated using (1) the entire available prey library ($n = 509$); (2) only Greenland prey, except for harp and hooded seals, as none were available from Greenland ($n = 333$); and (3) only Greenland prey and only ringed seal from 2002, 2004 or 2006 (the main prey item, and also the prey for which we had the most temporal variation).

Additional statistical analysis

Statistical analysis was performed using Statistica version 10 (Statsoft, Tulsa, OK, USA), and deemed statistically significant at $P < 0.05$. The potential influence of sample oxidation on QFASA-generated polar bear diet estimates was assessed by excluding samples with obviously low 22 : 6n-3 values (the longest chain, most unsaturated FA analyzed, and thus most subject to oxidation; Fig. S1) and by running a permutation MANOVA on the subsequent dataset including subjective oxidation class as a factor (Appendix S1). Next, a permutation MANOVA was run 10 000 times using the Bray–Curtis distance matrix to test for diet differences between age/sex classes, years, seasons, and all first-order interactions (adonis function in vegan package in R). *Post hoc* differences between age/sex classes were tested by one-way ANOVA, followed by Tukey's HSD for unequal n.

Diet and δ^{13}C-FA temporal trends were assessed by simple linear regression on yearly mean prey proportions or δ^{13}C-FA ratios. Differences in polar bear and ringed seal δ^{13}C-FAs were assessed using Student's *t*-tests. For diet trends, statistical analysis was also run on arcsin-transformed diet estimates since values were proportional data, however, the results did not differ. Relationships of climate indexes to yearly mean diet estimates were analyzed by simple linear regression. For all linear models, residual analysis was used to test for outliers (>2 SD) and for normality and homogeneity of the residual variances.

The influence of changing diet on POP trends was determined by comparing the annual change (%) in POP concentrations before and after diet correction (McKinney *et al.*, 2009). Briefly, trends were initially calculated by simple linear regression of yearly mean log-transformed POP concentrations vs. year. Annual change was calculated as $(1 - 10^b) \times 100\%$, where b is the slope. Diet-corrected trends were determined similarly, but included ringed seal consumption as a covariate. First, the model log-POP = year + ringed seal + year × ringed seal was analyzed. When the interaction term was not significant, data were reanalyzed according to log-POP = year + ringed seal. Least-squares annual mean POP concentrations adjusted to 1984 ringed seal consumption levels were determined to demonstrate what the POP trends would be had the diet not changed since 1984 (first year in the time series). A simple linear regression of adjusted means vs. year was performed, and the slope b was used to determine diet-adjusted annual change. To assess whether annual change differed before and after diet correction, the slopes of the two regressions were compared by Student's *t*-tests. We focused on subadult bears due to significant differences in

POP concentrations between sex/age classes and because subadults were most numerous and previously showed the largest number of significant POP trends (Dietz *et al.*, 2013a,b). Unadjusted trends were slightly different than previously reported as not all bears with POP data were also assessed for FAs, newer 2011 EG samples were included, yearly log-mean (not log-median) POP concentrations were used to calculate trends, and year was considered as February–December plus January of the following year as for the diet analysis. Regardless, relative trends before and after diet correction were the focus here, as detailed POP trend results were described previously (Dietz *et al.*, 2013a,b).

Results

Polar bear and prey fatty acid signatures

Sixty-nine FAs were monitored in 310 EG polar bear adipose samples, and that of their prey, and of these, 62 were reliably quantified in all samples (Table S1). The 31 FAs comprising the 'dietary' FA subset, those FAs solely or primarily present from direct dietary uptake (Iverson *et al.*, 2004), were used in subsequent diet modeling. Polymethylene-interrupted FA were also screened as markers of specific diet items (bearded seal, walrus), but none were reliably quantified, unlike in Canadian polar bear subpopulations (Thiemann *et al.*, 2007).

Potential confounding factors in polar bear diet estimates

The profile of selected dietary FAs was compared between the prey library in this study, comprised of EG and Davis Strait prey (selected data from Thiemann *et al.*, 2008a,b), and published prey data from similar regions collected at different time points (Falk-Petersen *et al.*, 2009) (Fig. S2). For most FAs, the between-species differences were consistently larger than within-species variation related to spatial and temporal differences in prey collection. The prey library from the current study was also subjected to a hierarchical cluster analysis based on average dietary FA values between prey types and collection region/time period (Fig. 1). Prey consistently formed clusters based on species, not on collection location or time period (although harp and hooded seal showed more similarity than other species).

Prey-on-prey and diet simulation modeling results indicated the robustness of the QFASA modeling for this dataset. In the prey-on-prey simulations, the six prey species were generally well distinguished from one another based on their FA signatures (Fig. 2). Bearded seal, harp seal, narwhal, ringed seal, and walrus were well distinguished from one another. Hooded seal was correctly identified 79% of the time, with 14% misidentified as harp seal. Thus, the prey species should be well distinguished as EG polar bear dietary items, although with likely a small number of misidentifications between harp and hooded seals. In the diet simulations, the 'pseudo-bear' diet was well estimated from the 'prey' dataset (Fig. 3), indicating that QFASA was able to determine a given EG polar bear diet with a good degree of accuracy and precision. Running QFASA multiple times using different prey library compositions showed that estimated EG polar bear diets were similar regardless of temporal or spatial variation in prey library composition (Fig. S3). Overall, these findings suggest that EG diet estimates were not largely biased by using prey collected in different years and (neighboring) locations than polar bear collections.
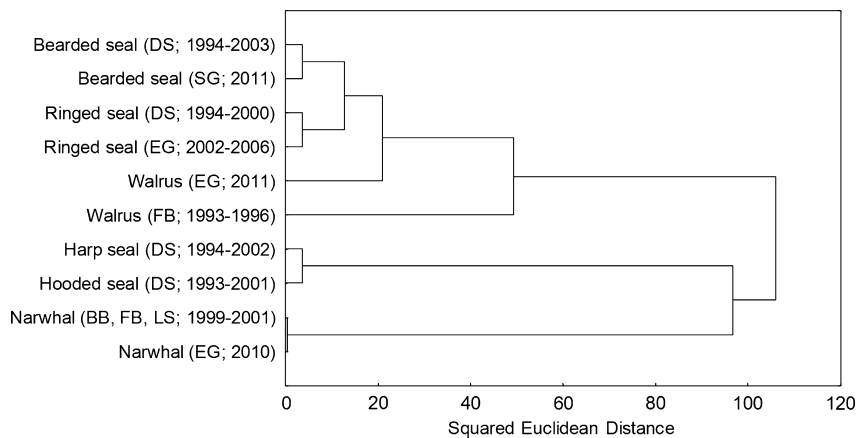
Fig. 1 Hierarchical cluster analysis based on averages of all dietary fatty acids (mass%) from bearded seal, harp seal, hooded seal, narwhal, ringed seal, and walrus blubber, grouped by species and collection location/year. Analysis was based on the full prey library used to generate EG diet estimates. Location abbreviations are as follows: DS, Davis Strait; SG, South Greenland; EG, East Greenland; FB, Foxe Basin; BB, Baffin Bay; LS, Lancaster Sound.
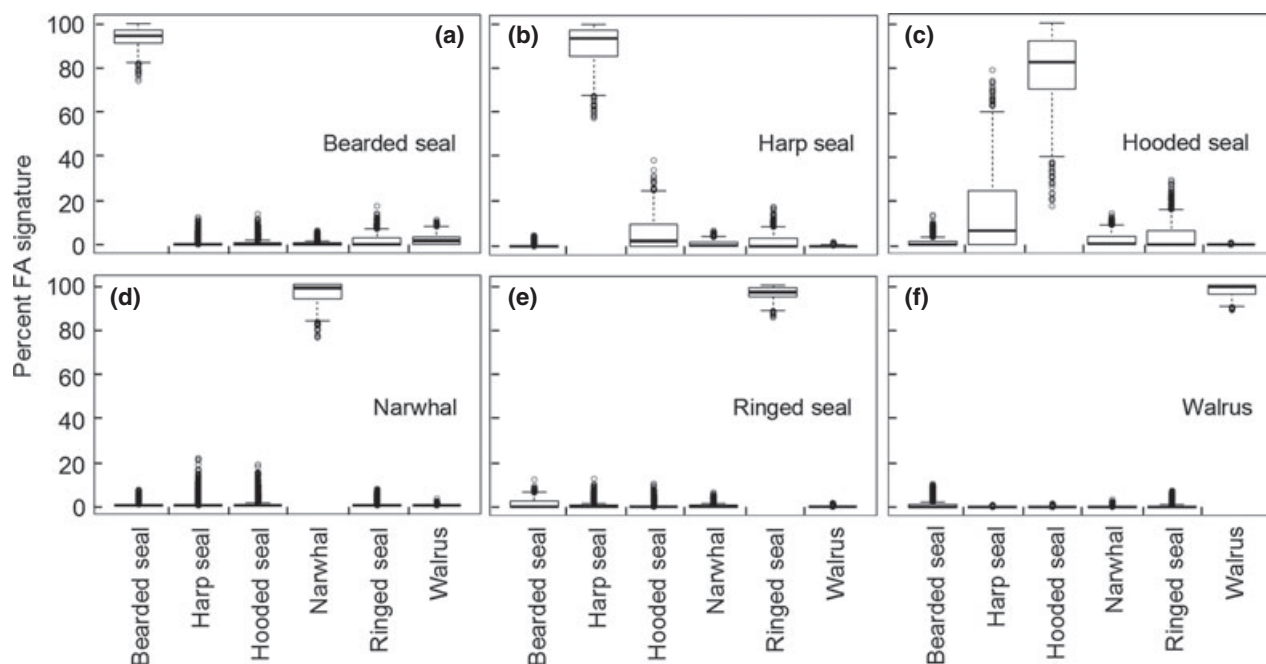
Fig. 2 Prey-on-prey simulation results for (a) bearded seal, (b) harp seal, (c) hooded seal, (d) narwhal (e) ringed seal and (f) walrus. Box-and-whisker plots are shown, wherein the box contains the 25th and 75th percentile ranges, the middle line represents the median, the whiskers extend to 1.5 times the interquartile range, and circles represent outliers beyond this range. Results indicate how well each prey species is distinguished from the others based on fatty acid signatures.
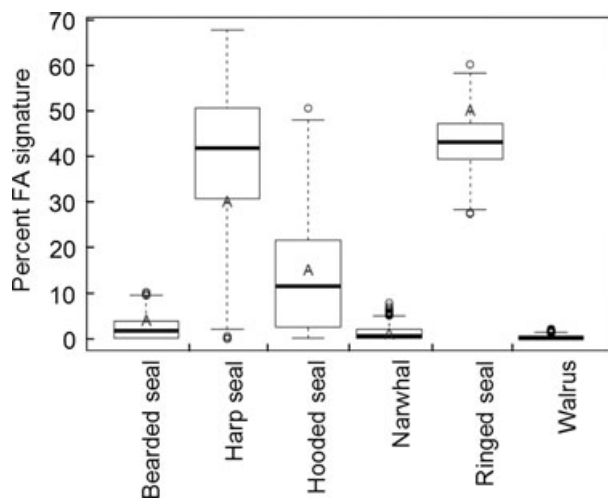
Fig. 3 Diet simulation results for East Greenland polar bears. A box-and-whisker plot is shown, wherein the box contains the 25th and 75th percentile ranges, the middle line represents the median, the whiskers extend to 1.5 times the interquartile range, and circles represent outliers beyond this range. The simulation randomly divides the prey into a 'simulation' and a 'prey dataset. The assigned 'pseudo-bear' signature (indicated by the letter A) was set to 4% bearded seal, 30% harp seal, 15% hooded seal, 1% narwhal, 50% ringed seal, and 0% walrus, and the simulation results indicated by the box plots closely reproduced the assigned signature.

Nonetheless, our analysis of prey from different years was limited. Therefore, we cannot fully discount the possibility that our diet estimates could additionally be influenced by changing diets of the marine mammal prey themselves. Assessing this explanation would require extensive archived samples of all prey species over the past three decades, which are not available. Finally, our diet estimates were not significantly influenced by potential sample oxidation (Appendix S1; Fig. S1).

Polar bear diets

Over the entire study period, EG polar bears fed mainly on ringed (47.5 ± 2.1%), harp (30.6 ± 1.5%), and hooded seal (16.7 ± 1.3%) (Fig. 4a). Bearded seal (4.5 ± 0.3%), narwhal (0.7 ± 0.2%), and walrus (0.0 ± 0.0%) consumption was minor or not detectable.

Sex/age differences in polar bear diets

Estimated diets of EG polar bears were influenced by sex/age class (permutation MANOVA; $P < 0.001$; Fig. 4b). Adult females and subadults consumed higher proportions of ringed seal compared to adult males (*post hoc* Tukey's test; $P < 0.001$), whereas adult males consumed more harp seal than females and subadults
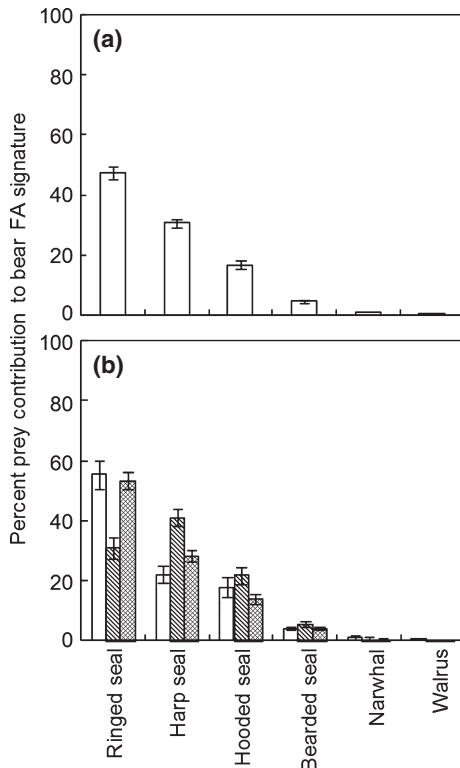
Fig. 4 Diet estimates for (a) all East Greenland polar bears and (b) for East Greenland adult female (white bars), adult male (striped bars), and subadult (cross-hatched bars) polar bears, generated by QFASA from adipose tissues collected from 1984 to 2011. Error bars represent ± SE of individual polar bear diet estimates.

($P < 0.001$, $P = 0.002$, respectively). Proportions of the minor dietary items, bearded seal, narwhal, and walrus did not differ between sex/age classes ($P > 0.25$).

Seasonal and inter-annual differences in polar bear diets

Estimated diets of EG polar bears varied by year (permutation MANOVA; $P = 0.005$; sample sizes by year found in Table S2). There were no overall diet differences between spring-summer and fall-winter sampled bears ($P > 0.25$), however, the season × year interaction was significant ($P = 0.02$). That is, EG polar bear diets changed from 1984 to 2011, but time trends differed between spring-summer and fall-winter sampled bears. Therefore, time trends were analyzed separately by season.

For spring-summer 1984–2011 sampled bears, yearly mean hooded seal consumption linearly increased ($r^2 = 0.48$, $P < 0.001$, $n = 23$ years; 9.5%/decade; $0.0 ± 0.0\%$ in 1984 to $25.9 ± 9.1\%$ in 2011), ringed seal consumption decreased ($r^2 = 0.28$, $P = 0.01$;

14%/decade; $90.1 ± 2.5\%$ in 1984 to $33.9 ± 11.1\%$ in 2011), and proportions of other prey species did not change ($P > 0.23$) (Fig. 5). When time trends for spring-summer sampled bears were analyzed separately for each age/sex class, we found similar increases and decreases, though not as many were significant likely due to lower numbers of samples per year and years analyzed. Hooded seal increased in diets of adult males sampled in spring-summer ($r^2 = 0.36$, $P = 0.01$, $n = 16$ years; 17%/decade). For fall-winter 1986–2009 sampled bears, there were no significant diet trends ($P > 0.12$, $n = 18$ years) (Fig. S4). Separate analysis of time trends for fall-winter sampled bears by sex/age class similarly showed no diet changes ($P > 0.09$, $n = 11, 8, 15$ years for adult females, males, and subadults, respectively).

*Fatty acid carbon isotope patterns and time trends in polar bears and ringed seals*

The $\delta^{13}C$ ratios of eight major FAs (14:0, 16:0, 16:1n-7, 18:1, 20:1, 22:1, 20:5n-3, and 22:6n-3) were determined with acceptable accuracy and precision for EG polar bears. All except 22:1 were also acceptably determined in EG ringed seals. Concentrations of other important dietary FAs, including C_{18} polyunsaturated FAs, were too low to provide acceptable values. Mean $\delta^{13}C$-FAs varied widely from $-39.32 ± 0.11‰$ to $-29.74 ± 0.07‰$ in polar bears and from $-37.81 ± 0.17‰$ to $-32.16 ± 0.15‰$ in ringed seals (Fig. 6). Polar bear FAs were ^{13}C-enriched relative to ringed seal FAs ($F_{1,91} > 8.5$, $P < 0.004$), except for 20:5n-3, which was depleted ($F_{1,91} = 24.3$, $P < 0.001$) in bears relative to seals. Within FA groups of the same degree of unsaturation, $\delta^{13}C$ increased with chain length, suggesting that de novo synthesis of longer chain FAs, which would result in $\delta^{13}C$-depleted products, was not a major factor in $\delta^{13}C$-FA values. For spring-summer sampled bears from 1990 to 2010, yearly mean $\delta^{13}C$ ratios declined for the FAs 18:1 ($r^2 = 0.88$, $P < 0.001$, $n = 9$ year) and 20:1 ($r^2 = 0.84$, $P < 0.001$) (Fig. 7). Time trends were not observed for any $\delta^{13}C$-FAs in fall-winter sampled bears from 1986 to 2009 ($P > 0.01$ (Bonferroni-corrected $\alpha = 0.006$), $n = 9$ year).

Relationship of polar bear diet trends to climate indexes

In spring-summer sampled bears from 1984 to 2011, hooded seal consumption was negatively correlated with yearly mean NAO ($r^2 = 0.29$, $P = 0.009$), but not with Greenland Sea ice area. Ringed seal consumption in spring-summer sampled bears increased with NAO, but the correlation was not significant ($r^2 = 0.14$, $P = 0.08$). Thus, in years of more negative NAO, diets of spring-summer sampled EG polar bears were higher
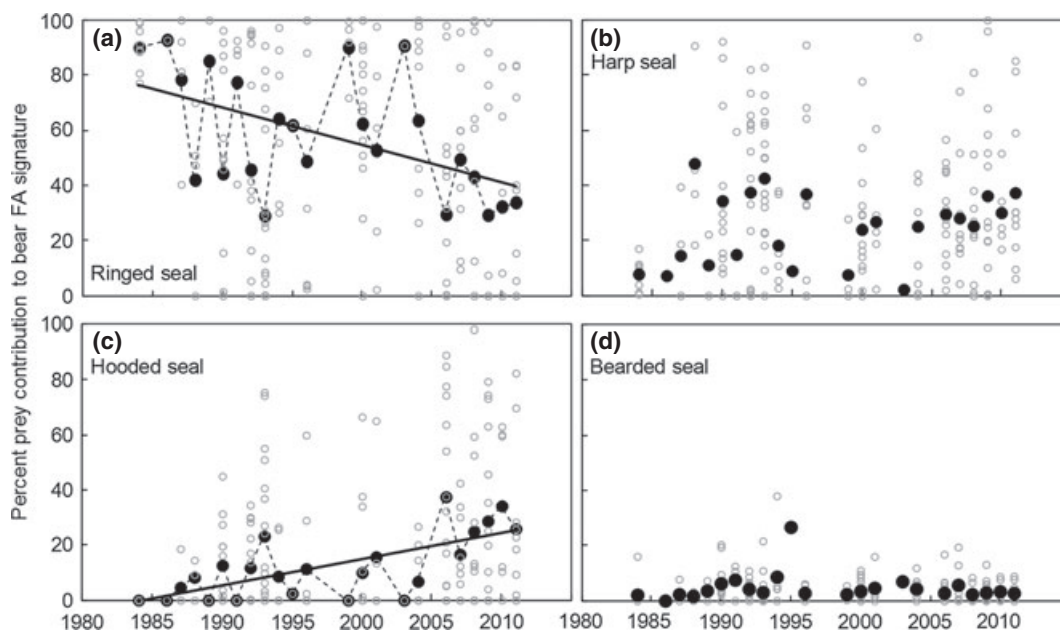
Fig. 5 Percent contribution to East Greenland polar bear yearly mean (●) and individual (○) diets from spring-summers of 1984–2011 of the following prey species: (a) ringed seal (overall mean 48.9%) (b) harp seal (29.3%), (c) hooded seal (16.9%) and (d) bearded seal (3.9%). Narwhal and walrus data not shown as they were almost never consumed and showed no temporal trends. Linear regression lines are provided for statistically significant time trends only.
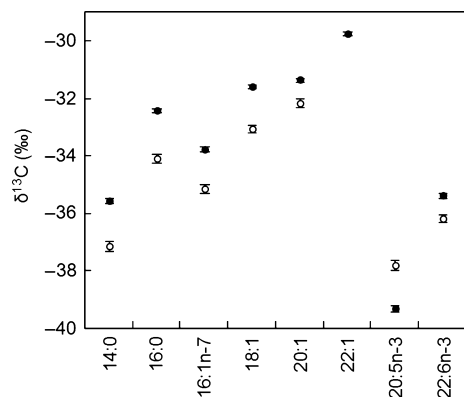
Fig. 6 The $\delta^{13}C$ ratios of individual fatty acids in East Greenland polar bears (●) collected from 1986 to 2010 and ringed seals (○) collected from 2002 to 2006. Ringed seal 22:1 data not shown as concentrations were too low to provide accurate $\delta^{13}C$ data. Error bars represent ± SE.

in hooded seal and lower in ringed seal. We note, however, that both NAO and Greenland Sea ice area were negatively correlated with year during the study period ($r^2 = 0.26$, $P = 0.006$ and $r^2 = 0.29$, $P = 0.004$, respectively), and therefore, year and climate indexes may explain some overlapping components of variation in the diet estimates, i.e., the separate contribution of year and climate to diet estimates was not fully distinguishable.
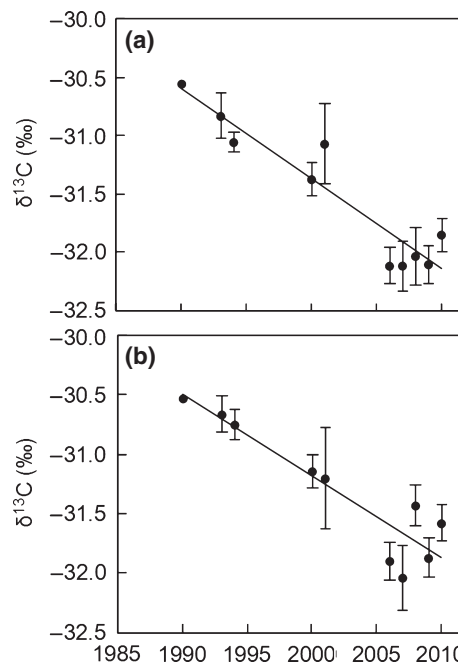

Fig. 7 Yearly mean $\delta^{13}C$ ratios for the individual fatty acids (FAs) 18:1 (a) and 20:1 (b) for East Greenland polar bears from spring-summers of 1990–2010. Linear regression lines indicate significant time trends. Error bars represent ± SE. No significant time trends were found for $\delta^{13}C$ ratios of the FAs 14:0, 16:0, 16:1n-7, 22:1, 20:5n-3, and 22:6n-3 (data not shown).

Influence of polar bear diet changes on POP trends

We examined the impacts of diet changes on POP trends in EG subadult bears by comparing trends before and after adjusting for diet change. The year × ringed seal interaction was significant for α-HCH, dieldrin, and heptachlor epoxide ($P < 0.007$), so these POPs were not further considered. For all other POPs, the regression was rerun without the interaction term. Year was significant in all cases ($P < 0.006$), explaining 28–61% of the variance (partial η^2). Ringed seal consumption was also significant ($P < 0.03$), explaining 3.6–26% of the variance (except for $\sum$DDT and p,p'-DDE).

In EG bears, prior to adjusting for diet changes, concentrations of all chlorinated POPs except HCB showed significant annual declines averaging 3.0% (range: 1.7% for OCS to 5.0% for $\sum$DDT) (Dietz *et al.*, 2013b; Fig. 8). Concentrations of more recently produced PBDEs showed annual increases averaging 3.5% (range: 3.0% for $\sum$PBDE to 4.1% for BDE153), although levels of certain PBDE congeners have peaked recently (Dietz *et al.*, 2013a). After diet adjustment, annual declines were still significant for all chlorinated POPs except HCB. Decline rates were slightly faster though similar, averaging 3.2% yr^{-1} (range: 1.9% for OCS to 4.9% for $\sum$DDT) (Fig. 8). Rates of increase in brominated POP concentrations were slightly slower though similar after adjusting for diet change, averaging 3.2% yr^{-1} (range: 2.8% for $\sum$PBDE to 3.6% for BDE153). Although the change in
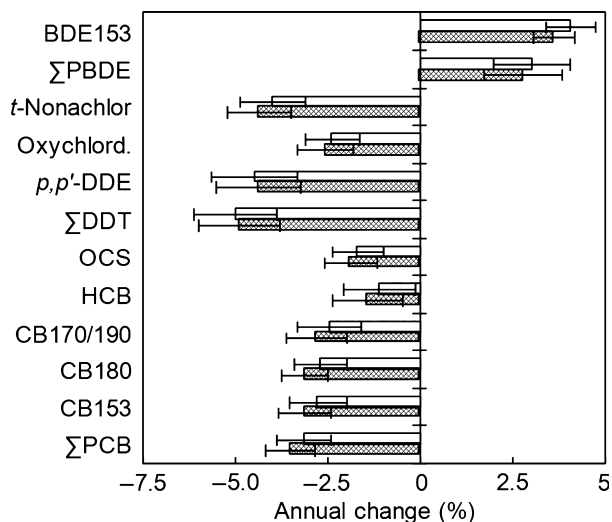
Fig. 8 Annual% change (±SE) in East Greenland polar bear adipose contaminant concentrations prior to (white bars) and after controlling for the influence of diet (cross-hatched bars). Trends controlling for diet were calculated by including ringed seal consumption (dietary%) as a covariate in the regression model, and generating the least squares means adjusted to 1984 ringed seal consumption.

slope between the unadjusted and diet-adjusted trends was not significant for any POPs ($P > 0.62$), the unadjusted decline rates for chlorinated POPs were consistently slower (other than $\sum$DDT and p,p'-DDE for which ringed seal was not a significant covariate) than the diet-adjusted rates (by an average of 12%) and consistently faster for brominated POPs (by an average of 9%).

Discussion

Overall, FA analysis showed that EG polar bear diets were comprised mainly of ringed seal, consistent with FA and bulk stable isotope analysis of Alaskan and Canadian Arctic and subarctic polar bear diets (Bentzen *et al.*, 2007; Thiemann *et al.*, 2008a). Our QFASA diet estimates represent the proportional biomass of each prey species consumed, i.e., the proportional number of individual ringed seals consumed could be higher, as ringed seals are substantially smaller than the other prey species (Iverson *et al.*, 2006; Thiemann *et al.*, 2008a). Nonetheless, the biomass contribution to the diet is the most relevant from the perspective of energy intake, as well as contaminant uptake. Harp and hooded seal consumption was also substantial, similar to reported diets of Davis Strait polar bears (Iverson *et al.*, 2006; Thiemann *et al.*, 2008a). High harp and hooded seal consumption in both EG and Davis Strait polar bears relative to other subpopulations is likely due to access to large populations of these seals, whose habitat ranges are restricted to within the North Atlantic and proximate arctic waters (reviewed in Laidre *et al.*, 2008). The Greenland Sea harp seal population, so named due to their whelping/breeding areas, is currently estimated at around 700 000 individuals (ICES, 2011). Although hooded seals are managed as two stocks according to breeding/whelping areas, they are considered one panmictic population (Coltman *et al.*, 2007). EG polar bears have access to Northeast Atlantic hooded seals during breeding/whelping in March, and to both stocks during June/July molting which takes place in the Denmark Strait and the Greenland Sea for the Northwest and Northeast Atlantic stocks, respectively (Andersen *et al.*, 2009; Frie *et al.*, 2012). Harp and hooded seals are less wary than other seals of being approached by humans or polar bears, and outside of whelping/breeding seasons, often haul out on the ice in groups (Stirling & Parkinson, 2006). Indeed, there are several reports of polar bears targeting these seals off the EG coast at large aggregation sites (Wiig *et al.*, 2003). Bearded seals and narwhals also occur at the pack ice edge in the summer (Born *et al.*, 1997), but are not frequently consumed based on our diet estimates, presumably because they are more difficult to capture relative to harp and hooded seals.

Female and subadult EG bears consumed more small-bodied ringed seals, whereas adult males consumed more large-bodied harp and hooded seals. Adult female and subadult polar bears are much smaller than adult males and are therefore not as likely to target larger prey species to the same extent. These findings are consistent with Canadian polar bear subpopulations, wherein larger prey were consumed by older and/or male bears more frequently than younger and/or female bears (Thiemann et al., 2008a). These authors concluded that these demographic differences were likely driven by different energetic requirements, reduced within-species competition, and differences in habitat ranges. Greater consumption of harp and hooded seals by adult male EG bears is consistent with findings in other areas where they forage further offshore to a greater extent (Stirling et al., 1993), which would overlap more with the whelping and molting areas of these seals. Although adult females with cubs-of-the-year may still be denning during part of the harp and hooded seal whelping/breeding periods, tracking data from two central EG adult female polar bears indicated that they did inhabit these offshore areas in spring to late-summer (Wiig et al., 2003). Therefore, these subarctic seals may be an important food resource across demographic groups.

Long-term changes in diets of spring-summer sampled EG polar bears, but not in fall-winter sampled bears, are consistent with polar bear feeding behavior. Access to young, naïve seal pups of multiple species and to hauled-out adult hooded and harp seals occurs mainly in the spring-summer. These subarctic seals are highly migratory and only available to EG polar bears during breeding/molting periods in the spring/summer (Folkow et al., 1996, 2004; Wiig et al., 2003). Polar bears generally have less access to prey and consume less during fall-winter, as reflected by body condition differences between seasons (Stirling et al., 2008). Nonetheless, our dataset contained lower numbers of years/samples from fall-winter, and thus may not have been as sensitive to potential feeding changes during fall-winter.

Although ringed seals were the main prey item overall, when examined temporally, diets of EG polar bears shifted from mainly this arctic seal species in the early 1980s to mainly subarctic seal species (harp and hooded seals combined) in more recent years. These results suggest upper food web changes within this ecosystem as the climate has warmed and the sea ice has declined over the past three decades (Perovich & Richter-Menge, 2009). As harp and hooded seal whelping grounds are mainly found along the eastern ice edge off EG, ice reductions mean shorter distances from land where females and newborn cubs are denning (Wiig et al.,

2003; Frie et al., 2012). Historical hunting statistics from West Greenland showed comparable harp seal increases and ringed seal declines during a warm period in the 1920s, as sea ice conditions changed and ringed seal prey items like Arctic cod moved northward and Atlantic cod invaded (reviewed in Laidre et al., 2008). Hunting records for Ittoqqortoormiit from the 1980s–2010s, however, are limited (Appendix S1). The Greenland Sea harp and Northwest Atlantic hooded seal populations are currently below historical levels but have increased in recent decades; Northeast Atlantic hooded seal populations are also below historical levels, but have not substantially increased and possibly have even declined in the last decade (Salberg et al., 2008; ICES, 2011; Frie et al., 2012). It was not possible from our data to determine the relative contribution of the Northwest and Northeast Atlantic hooded seal stocks to increased hooded seal consumption in EG polar bears; future analysis of Northwest and Northeast Atlantic hooded seal FA and POP profiles may be helpful in distinguishing these stocks. We are unaware of any data supporting ringed seal population declines or changes in distribution in this area, other than that implied from changes in EG polar bear diets. Unlike changes observed in ringed seal consumption, we found no evidence of temporal change in consumption of another arctic seal species, the bearded seal. Bearded seals tend to use pack ice habitat, whereas ringed seals rely more on land-fast ice (Laidre et al., 2008). It may be that if EG polar bears are hunting more at the pack ice edge, they still have reasonable access to bearded seals and thus similar, albeit low, consumption levels over time.

Fatty acid isotope analysis is not yet commonly applied to diet studies, and work is needed to determine species-specific diet-tissue ^{13}C-fractionation factors for FAs of interest in quantitative diet studies (Bec et al., 2011). Nonetheless, the δ^{13}C-FA patterns and time trends examined here support QFASA-estimated diet trends and further contribute to the application of this approach in future studies. Variation in δ^{13}C values among individual FAs is due to isotopically different diet sources for each FA and/or differential ^{13}C-fractionation during desaturation or chain elongation reactions (Gilmour et al., 1995). Carnivorous mammals are capable of only minor amounts of FA chain desaturation/elongation, and since polar bears have a high lipid diet, there is likely little need or ability for them to synthesize FAs de novo (Stirling & McEwan, 1975; Gilmour et al., 1995 and references therein). Indeed, several lines of evidence suggest that the δ^{13}C-FA patterns monitored here were largely controlled by diet (Appendix S1). If observed temporal declines in δ^{13}C values of 18:1 and 20:1 largely reflect diet change, then our findings

could be interpreted to support a shift from more near-shore/benthic prey (and/or food web type) to more offshore/pelagic prey (Burton & Koch, 1999) from 1990s to 2010s. Alternatively, ice-algae are known to be significantly enriched in certain δ^{13}C-FA vs. pelagic phytoplankton (Budge *et al.*, 2008). Thus, the observed δ^{13}C declines could additionally indicate declines in the ice-associated food web as measured in these polar bears. These interpretations are consistent with greater feeding on hooded and/or harp seal, and/or an overall shift to a more pelagic food web in this region.

Our data also suggest improved sensitivity to detect change when δ^{13}C-FA analysis is used rather than when only bulk isotope and FA approaches are employed. Bulk isotope ratios represent the average δ^{13}C over all biomolecules present, which could have masked the declining δ^{13}C values we found for 18:1 and 20:1. Declines in these δ^{13}C-FAs were also very strong (more than 80% of variation in mean yearly δ^{13}C ratios were accounted for by year) relative to the QFASA-estimated diet change based on FA proportions (maximum 48% of variation in hooded seal consumption accounted for by year). Nonetheless, not all δ^{13}C-FA profiles changed over time, and further research is needed to determine the specific δ^{13}C-FA that will provide the most useful dietary information.

Polar bears from the EG subpopulation consumed more hooded seal and less ringed seal in years with lower NAO. Thus, periods with warmer temperatures and less ice in EG are suggested to result in conditions conducive to higher subarctic but lower arctic seal densities or accessibility to polar bears. We did not find a relationship of diets to Greenland Sea ice area. However, previous studies have found that large-scale climate indexes, such as the NAO, are frequently better predictors of ecological changes than more local climate indexes, like regional sea ice (Stenseth *et al.*, 2002). Nonetheless, year was a stronger predictor of ringed vs. hooded seal consumption than was NAO, suggesting that other factors are involved in the diet shifts and/or that NAO does not fully account for the climatic changes that are occurring in this region (Moritz *et al.*, 2002).

Ringed seal consumption was a significant factor in EG polar bear POP levels (other than ∑DDT and *p*, *p*′-DDE), implying differing levels of most POPs between ringed seals (for which consumption declined) and hooded seals (for which consumption increased). Thus, a portion of the overall slowly declining temporal trends for chlorinated POPs and increasing trends for brominated POPs was due to the EG polar bear dietary shift from less contaminated ringed seals to more contaminated hooded seals (and possibly harp seals, given the similarity in FA signatures between harp and hooded seals), rather than declines only being a consequence of declining environmental concentrations due to international regulations. Limited POP measurements reported for harp, hooded, and ringed seals collected from comparable locations and time periods support this interpretation. Hooded seals had substantially higher PCB, DDT, and CHL levels than harp seals in the Greenland Sea and also in the Gulf of St. Lawrence (Espeland *et al.*, 1997; Hobbs *et al.*, 2002), and harp seals have shown higher or similar legacy POP levels to ringed seals in the Barents Sea and in the White Sea (Kleivane *et al.*, 2000; Muir *et al.*, 2003). Previous work on western Hudson Bay polar bears also suggested a shift from arctic to subarctic seals in years with earlier sea ice breakup from 1991 to 2007, with consequently similar though more substantial impacts on POP time trends (McKinney *et al.*, 2009, 2010). For EG polar bears, legacy POP declines were slowed, but not reversed, by this diet change. The major driver of declining POP trends in EG polar bears was thus still related to controls on emissions/international regulations (Rigét *et al.*, 2010).

As one of the convergent ice subpopulations of polar bears, it has been predicted that EG polar bears will fare better in the short term, as multi-year ice changes to annual ice cover, than will divergent and seasonal ice polar bear subpopulations, such as in western Hudson Bay and the southern Beaufort Sea (Amstrup *et al.*, 2008, 2010; Stirling & Derocher, 2012). Our results suggest that EG bears are using subarctic seals as an increasingly important, albeit more contaminated, food resource. Adipose lipid content, an indicator of body condition (Thiemann *et al.*, 2006; Stirling *et al.*, 2008), has increased in EG polar bears over the same time period (M. McKinney, unpublished data). This finding suggests that EG individuals are currently in better condition than previously, possibly due to increased access to subarctic seals as a stable, reliable food source. Nonetheless, harp and hooded seal populations may decline in response to arctic climate change, as the pack ice that they seasonally require declines or breaks up earlier each year (Laidre *et al.*, 2008; Bajzak *et al.*, 2011; ICES, 2011). Thus, this additional food source, subsequent to declines in ringed seal in the diet, may only be a temporary one.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Appendix S1. Supplemental text covering methods of POP analysis, quality control, sample oxidation testing, and simulation exercises; results on the confounding influence of oxidation and simulation modeling; discussion regarding East Greenland hunting records, and evidence of dietary influence on fatty acid carbon isotopes.

Table S1. Adipose FA profiles of East Greenland polar bears collected from 1984 to 2011.

Table S2. Sample sizes for East Greenland polar bears collected from 1984 to 2011.

Figure S1. Percentage of 22:6n-3 in East Greenland polar bear adipose FA signatures, by subjective oxidation class.

Figure S2. Percentage of selected dietary fatty acids in the blubber of polar bear prey from Greenland and neighboring regions.

Figure S3. Influence on East Greenland polar bear QFASA-generated diet estimates of spatiotemporal variation in the prey library.

Figure S4. Proportional contribution of the prey species to East Greenland polar bear yearly mean and individual diets from fall-winters of 1986–2009.